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EMISSIONS OF AIR CONTAMINANTS FROM BOILERS AND PROCESS HEATERS

Howard Devorkin, et al

Joint District, Federal and State Project for the Evaluation of Refinery Emissions

June 1958

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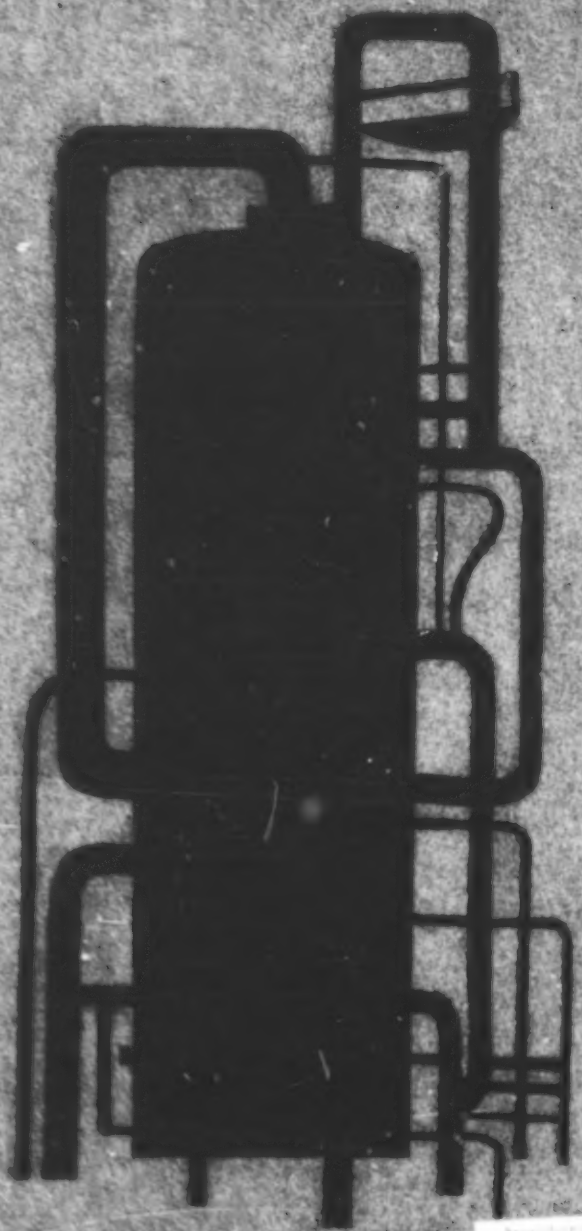

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REPORT NUMBER 7

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FOR THE EVALUATION OF REFINERY EMISSIONS

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by
HOWARD DEVORKIN
and
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Details of illustrations in this document may be better studied on microfiche.

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FOREWORD

In August 1955, the Los Angeles County Air Pollution Control District, the U. S. Public Health Service, and the California State Department of Public Health inaugurated the Joint District, Federal, and State Project for the Evaluation of Refinery Emissions in Los Angeles County. The Western Oil and Gas Association, representing the petroleum industry, also participated in the project. This report presents the results of one of the studies of the Joint Project.

TABLE OF CONTENTS

	Page
IN BRIEF	1
INTRODUCTION	2
STACK SAMPLING PROGRAM	4
SAMPLING PROCEDURES	6
Determination of Stack Gas Velocity	6
Determination of Stack Gas Volumes	9
Determination of Sampling Rate	9
Sampling Equipment	10
Outline of Sampling Method	10
OUTLINE OF ANALYTICAL METHODS	16
Alundum Thimble	16
Impinger Train (Water-HCl)	16
Whatman Paper Thimble	16
Impinger Train (NaOH)	17
Integrated Gas Sample for Orsat Analysis	17
Grab Samples	17
Fuel Analysis	17
DATA EVALUATION	18
Total Emissions from Boilers and Process Heaters	18

Page

Analytical Methods 19

Average Emission Factors 19

Relative Emissions from the Combustion of Oil and Gas ... 22

Comparison of Emissions from a Fume Burner and Boilers and Heaters 22

REFERENCES 24

APPENDIX 25

Analytical Method for Oxides of Sulfur 25

Analytical Method for Organic Acids 27

LIST OF TABLES

TABLE		Page
I.	DESCRIPTION OF BOILERS AND PROCESS HEATERS TESTED	5
II.	OXIDES OF NITROGEN, ALDEHYDES, HYDROCARBONS, ORGANIC ACIDS AND AMMONIA IN BOILER AND PROCESS HEATER STACK GASES	7
III.	SULFUR DIOXIDE, SULFUR TRIOXIDE, AND PARTICULATE MATTER IN BOILER AND PROCESS HEATER STACK GASES	8
IV.	AVERAGE EMISSIONS PER UNIT OF GASEOUS FUEL BURNED IN BOILERS AND PROCESS HEATERS	20
V.	AVERAGE EMISSIONS PER UNIT OF FUEL OIL BURNED IN BOILERS AND PROCESS HEATERS	21
VI.	TOTAL EMISSIONS FROM BOILERS AND PROCESS HEATERS IN REFINERIES IN LOS ANGELES COUNTY	22
VII.	RELATIVE EMISSIONS FROM BURNING OF OIL AND GAS	23
VIII.	COMPARISON OF EMISSIONS FROM BOILERS AND HEATERS AND A FUME BURNER	23

LIST OF FIGURES

FIGURE		Page
1	Conventional Box Type Heater	3
2	Cylindrical Vertical Heater	3
3	Source Testing Team and Equipment	11
4	Diagram of Sampling Train	12
5	Alundum Thimble and Thimble Holder	13
6	Alundum Thimble Sampling Train	13
7	Bottle for Collection of Orsat Sample.....	15
8	Grab Sample Bulb	15

IN BRIEF

Combustion of fuel oil and gas is a source of emissions to the atmosphere. This report details the techniques and results of a study to determine the extent of these emissions from combustion in oil refinery boilers and heaters in Los Angeles County.

A total of 21 stacks were sampled during the field testing program. These stacks serve 14 heaters, 10 boilers, and one fume burner. Average emission factors per unit of fuel used were calculated for each contaminant for combustion of both oil and gas. These emission factors were applied to the fuel used daily in boilers and heaters in all refineries to arrive at the following total emission figures:

Hydrocarbons, as hexane by I.R. (max.)	5 tons per day
Sulfur dioxide	72
Oxides of nitrogen, as NO_2	46
Particulate matter	5
Sulfur trioxide	2
Ammonia	negligible
Aldehydes, as HCHO (max.)	0.5
Organic acids, as acetic acid	3.5

INTRODUCTION

Many processes and operations in oil refineries use high pressure steam or require feed stock at elevated temperatures. A wide variety of boilers and process heaters are used to fill these needs. Although heaters may be of unique design, most units are the box type shown in Figure 1 or the cylindrical, vertical type illustrated in Figure 2. Boilers are generally of conventional design.

The fuel burned is refinery gas, purchased natural gas, or fuel oil, either singly or in combination. Refinery gas is a product of certain refining processes, particularly cracking and reforming. This gas contains hydrogen sulfide, originating from the cracking and hydrogenation of sulfur compounds in the petroleum distillate feed stocks.

In Los Angeles County, refinery gases are treated to remove large amounts of hydrogen sulfide for conversion to elemental sulfur or sulfuric acid. The fuel gas fed to the heaters may be either treated or untreated refinery gas, or purchased natural gas, or a mixture of any of them. The natural gas contains essentially no sulfur compounds. Treated refinery gas has practically all of the hydrogen sulfide removed. In some streams of fuel gas, containing untreated refinery gas, the concentration of hydrogen sulfide may reach 2 per cent, and in a few isolated instances, considerably higher.

Ordinarily, the refinery gas supplies about half of the industry's fuel needs, the remainder coming principally from purchased natural gas most of the year. In winter months, when residential heating demands sharply curtail natural gas deliveries to refineries, oil supplants most of the natural gas. The fuel oil used has a sulfur content of between 1 and 2 per cent by weight, but in some cases as much as 3 per cent.

The sulfur compounds in the fuel burned form sulfur oxides which are emitted to the atmosphere in the stack gases. Additionally, as a result of nitrogen fixation in the combustion process, oxides of nitrogen are found in the effluent gases. Other contaminants such as hydrocarbons, particulate matter, ammonia, aldehydes, and organic acids may also be present. This report details the techniques and conclusions of the Joint Project study of emissions from the combustion of fuel oil and gas in boilers and process heaters.

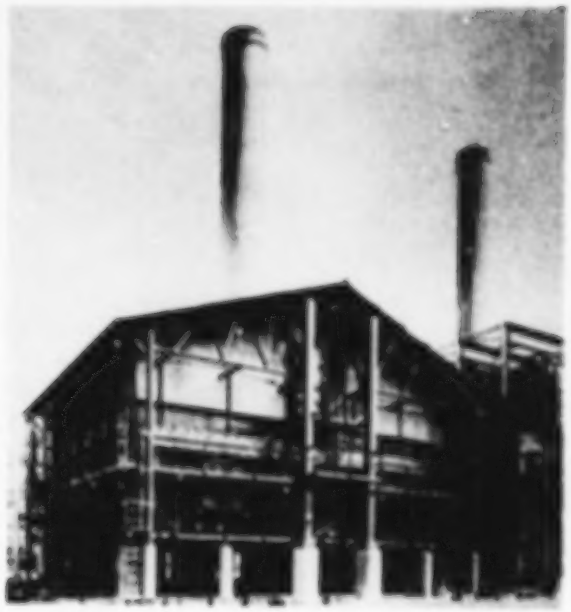

Figure 1. Conventional box type heater.

Figure 2. Cylindrical vertical heater.

In addition to boilers and process heaters, refineries often have fume burners which incinerate waste vapors and fumes from air blowing and stripping operations. Additional fuel is generally used to sustain combustion and no attempt is made to recover heat from these units. In number and size fume burners play a minor role in refinery combustion processes and this study did not attempt a separate estimate of emissions from these units. Test data were taken on a fume burner and these allowed a comparison of the relative combustion efficiency of these units with regular furnaces. Fumes or other combustible waste products are sometimes disposed of in boilers or process heaters.

Other types of combustion equipment found in refineries were not included in this study. These are catalyst regeneration vessels on catalytic cracking units, internal combustion engines which drive gas compressors, and wastes gas flares. Losses from this equipment have been detailed in other Joint Project reports (1, 2)*.

STACK SAMPLING PROGRAM

Field inspections were made of all heaters and boilers in all major refineries in the County. It was determined that nearly all units could be sampled for gaseous contaminants and that a few stacks had adequate sampling facilities for the measurement of particulate emissions. For particulate analysis the sample should be drawn from an area of stable velocity profile, usually high on the stack, so that isokinetic sampling conditions can be maintained (3).

In selecting the units for testing, an attempt was made to include a number of different types of boilers and heaters operating on both oil and gas. Aside from these considerations the units were selected for testing based on the availability of adequate sampling stations.

A total of 21 stacks were sampled during the field testing program. These stacks served 14 heaters, 10 boilers and one fume burner. Table I describes the units tested. Approximately 220 analyses were made on these

---

*Numbers in parentheses indicate references listed at the end of the report.

Table I

DESCRIPTION OF BOILERS AND PROCESS HEATERS TESTED

Unit No.	Type of Unit	Manufacturer	10^6 Btu/Hr.	Fuel Rates (Actual)		Burners			
				Gas	Oil	Oil		Gas	
				MCFH	GHP	Mfgr.	No.	Mgr.	No.
1	Cylind. Heater	Lummus	55	52.1	0		0	Coen	8
2	Box Heater	Alcorn	56.5	28.3	126	Alcorn	10	Alcorn	30
3	Cylind. Heater	Born	47.1	21.4	92.5	Zink	4	Zink	4
4	Box Heater	Braun	163	106	0	Coen	24	Zink	24
5	Cylind. Heater	Kellogg	133	118	0	Zink	4	Zink	72
6	Thermal Crack. Unit	Refinery Design	73	49.6	0		0	San Joaquin	290
7	Box Heater	Lummus	107	100	0	Peabody	4	Peabody	4
								Peabody	2
8	Two Box Heaters	Lummus	124.7	39	546	Zink	6	Zink	6
9	Two Box Heaters	Lummus	120.8	41.4	504	Zink	6	Zink	6
10	Cylind. Heater	Refinery Design	15.9	15.4	0		0	Coopus-Dennis	1
11	Box Heater	Foster Wheeler	49.3	51.1	0		0	Peabody	4
12	Box Heater	Foster Wheeler	47	46.2	0		0	Peabody	4
13	Two Boilers	Babcock & Wilcox	190	168	0	Peabody	4 ea.	Peabody	4 ea.
13A			190.8	60.7	756				
14	Two Boilers	Babcock & Wilcox	190	151	0	Peabody	4 ea.	Peabody	4 ea.
14A			200.8	84	700				
15	Boiler	Babcock & Wilcox	217	185	0	Peabody	4	Peabody	4
16	Boiler	Babcock & Wilcox	45	47.7	0	Peabody	4	Peabody	4
17	Boiler	Babcock & Wilcox	81	64.5	0	Leahy	5	Leahy	5
18	Boiler	Refinery Design	108.7	86.2	0	Peabody	4	Peabody	4
19	Fume Burner	Thorpe	9.4	8	0		0	Zink	2

units. All stacks were tested for the following gases:

Hydrocarbons	Aldehydes	Carbon monoxide
Sulfur dioxide	Organic acids	Carbon dioxide
Oxides of nitrogen	Oxygen	Nitrogen

In addition, a number of units were tested for particulate matter, sulfur trioxide, and ammonia.

Where possible the stack gas flow rate was determined directly by Pitot traverse. Where physical limitations or the location of the sampling station did not allow a direct measurement, the flow rate was calculated using stoichiometric principles. These techniques are described in detail in the SAMPLING PROCEDURES section of this report. The temperature of the gases in the stack or in the breeching was determined in all cases. The fuel rate and composition of the fuel were also obtained.

The results of the field testing program are shown in Tables II and III.

SAMPLING PROCEDURES

Determination of Stack Gas Velocity

In order to determine the total amount of stack emissions from the concentrations, it is necessary to determine the stack gas flow rates. For all stations where isokinetic sampling is to be performed (for particulate matter) gas velocities must first be determined (4).

Gas velocities were measured at all stations where adequate sampling holes in the stack could be provided in regions of fairly uniform flow. A Pitot tube (Type S or regular) was used with an inclined manometer reading velocity head in inches of water. A pyrometer was used to measure stack gas temperatures. To obtain the average gas velocity in the stack, the cross-sectional area of the stack is divided into a number of equal areas, and Pitot readings are made at the center of each area. For circular cross-section stacks, the equal areas are laid out in concentric circles.

Table II

OXIDES OF NITROGEN, ALDEHYDES, HYDROCARBONS, ORGANIC ACIDS, AND AMMONIA IN BOILER AND PROCESS HEATER STACK GASES

Unit No.	Fuel Usage		Stack Gas		Excess Air	Nitrogen Oxides as NO_2		Aldehydes as HCHO*		Hydrocarbons as hexane by I. R. *		Organic Acids as acetic acid		Ammonia	
	Gas MCFH	Oil GPH	Flow SCFM	Temp. °F.	%	ppm.	lb. /hr.	ppm.	lb. /hr.	ppm.	lb. /hr.	ppm.	lb. /hr.	ppm.	lb. /hr.
1	52.1	0	15,300	410S	56	396	44.2	2	0.1	8	1.7	0.6	0.1	2.2	0.09
2	28.3	126	14,000	970B	46	127	13	4	0.2	9	1.7	4.1	0.5	nm	nm
3	21.4	92	8,800	670S	19	132	8.5	6	0.2	8	1	29	2.4	0.06	0.002
4	106.0	0	30,000	nm	15	93	20	1	0.3	7	4	5	1.4	nm	nm
5	118.0	0	34,000	860B	61	91	22.3	1	0.3	5	2	4	1.2	nm	nm
6	49.6	0	16,000	1300B	81	83	9.7	1	0.1	10	2.2	7	1.1	Nil	Nil
7	100.0	0	27,000	800B	64	97	19	1	0.2	10	3.7	7.2	1.9	1	0.07
8	39.0	546	19,500	940S	56	214	30	9	0.8	10	2.7	14	2.5	Nil	Nil
9	41.4	504	22,000	900B	69	206	33	4	0.4	10	3	22	4.5	Nil	Nil
10	15.4	0	4,500	860S	160	36	1.2	1	0.1	5	0.3	12	0.5	0.4	0.005
11	51.1	0	12,000	900B	68	34	3.0	1	0.1	5	0.8	6	0.7	nm	nm
12	46.2	0	12,000	850B	100	34	3.0	1	0.1	5	0.8	18	2	nm	nm
13	168.0	0	45,000	520S	55	93	30.5	1	0.4	5	3	2	0.8	nm	nm
13A	60.7	756	44,700	540S	65	231	75	2	0.4	8	5	8.3	3.5	2.3	0.28
14	151.0	0	40,200	510S	17	168	49	1	0.2	7	4	8.7	3.3	0.5	0.05
14A	84.0	700	52,000	540S	38	242	91	1	0.4	5	3	43	21.4	0.6	0.08
15	185.0	0	47,000	330B	76	137	46.7	3	0.7	8	5	0.9	0.4	Nil	Nil
16	47.7	0	9,000	530B	52	70	4.6	1	0.8	10	1.2	4	0.3	Nil	Nil
17	64.5	0	21,000	430S	110	120	18	1	0.2	8	2	15	3.1	nm	nm
18	86.2	0	20,000	700S	29	108	16	1	0.2	8	2	3.4	0.7	nm	nm
19	8	0	6,800	940S	nm	12	0.6	77	2.5	45	4.2	49	3.1	0.2	0.004

* Some of the concentrations were below the sensitivity of the analytical technique, and the emissions are maxima.
S = stack temperature
B = breeching temperature
nm = not measured

Table III

SULFUR DIOXIDE, SULFUR TRIOXIDE, AND PARTICULATE MATTER IN BOILER AND PROCESS HEATER STACK GASES

Unit No.	Fuel Usage		Stack Gas		Excess Air %	SO_2		SO_3		Particulates	
	Gas MCFH	Oil GPH	Flow SCFM	Temp. °F.		ppm.	lb./hr.	ppm.	lb./hr.	gr./SCF.	lb./hr.
1	52.1	0	15,300	410S	56	51	7.9	1.1	0.2	0.013	1.7
2	28.3	126	14,000	970B	46	593	84	11.7	2.1	nm	nm
3	21.4	92	8,800	670S	19	238	21.3	0.5	0.05	0.060	4.6
4	106.0	0	30,000	nm	15	35	10.5	nm	nm	nm	nm
5	118.0	0	34,000	860B	61	93	32	nm	nm	nm	nm
6	49.6	0	16,000	1300B	81	11	1.8	Nil	Nil	nm	nm
7	100.0	0	27,000	800B	64	63	17.3	nm	nm	nm	nm
8	39.0	546	19,500	940S	56	191	37.8	13.7	3.4	nm	nm
9	41.4	504	22,000	900B	69	232	51.7	8.1	2.2	nm	nm
10	15.4	0	4,500	860S	160	373	17.1	27.1	1.5	0.027	1.1
11	51.1	0	12,000	900B	68	513	62	24.9	3.8	nm	nm
12	46.2	0	12,000	850B	100	497	61	21.2	3.3	nm	nm
13	168.0	0	45,000	520S	55	105	47.9	nm	nm	nm	nm
13A	60.7	756	44,700	540S	65	358	162	11	6	0.035	13.5
14	151.0	0	40,200	510S	17	298	122	3.1	1.6	0.005	1.8
14A	84.0	700	52,000	540S	38	323	171	3.8	2.5	0.032	14.2
15	185.0	0	47,000	330B	76	7	3.4	Nil	Nil	nm	nm
16	47.7	0	9,000	530B	52	3	0.3	Nil	Nil	nm	nm
17	64.5	0	21,000	430S	110	296	63	7.9	2.1	nm	nm
18	86.2	0	20,000	700S	29	363	74	6.4	1.6	nm	nm
19	8	0	6,800	940S	nm	90	6.2	0.5	0.04	nm	nm

S = stack temperature
B = breeching temperature
nm = not measured

The gas velocity at each point in the Pitot traverse is given by:

$$V = 2.90F \sqrt{\frac{29.92}{P} \times \frac{1.00}{D} \times HT}$$

where

V = velocity, feet per second
F = Pitot tube factor (F = 1.00 for the standard Pitot tube)
(F = 0.835 for the Type S Pitot tube)
P = stack gas pressure, inches of mercury absolute
D = specific gravity of stack gas referred to air
H = draft gauge reading, inches of water
T = stack gas temperature, degrees Rankine

Three complete traverses are averaged to give the average stack gas velocity at the sampling station.

Determination of Stack Gas Volumes

When the average gas velocity has been determined, the gas volume can be calculated using the cross-sectional area of the stack.

A large amount of sampling, however, was performed from stations located in the breechings to the stacks, since no suitable stack sampling locations were available. Under these conditions no average gas velocity measurements were possible due to the irregular flow patterns and the insufficient sample hole access to these large ducts. As a consequence, gas volumes in these cases were calculated from fuel consumption data and analyses of the stack gases for CO_2 and H_2O.

Determination of Sampling Rate

For all cases where particulate matter was to be sampled, a convenient point of near-average velocity at the sample station was selected as the sample point. A sample nozzle diameter was selected to yield an isokinetic sampling rate in the range of 0.5-1.0 CFM. A convenient equation to determine the conditions of isokinetic sampling is:

$$M = 0.33 \left(\frac{T_m}{T_s}\right) V d^2 \left(\frac{P_s}{P_m}\right) \left(\frac{100 - W}{100}\right)$$

where

M = meter sample rate, CFM
T_m = meter temperature, degrees Rankine
T_s = stack temperature, degrees Rankine
V = velocity of stack gases at sample point, feet per second
d = diameter of sample nozzle, inches
P_s = static pressure in stack, inches of mercury absolute
P_m = pressure at meter, inches of mercury absolute
W = estimated water vapor content of stack gases, volume per cent

Sulfur trioxide was also sampled isokinetically in those cases where particulate matter was sampled. The usual breeching temperatures, however, were high enough to consider the SO_3 being sampled at these locations to be gaseous at the sample probe, making isokinetic sampling unnecessary. Sampling rates ranged in these cases from 0.5 to 0.8 CFM.

Sampling Equipment

The following items of equipment were required for a complete test per station (see Figure 3):

Glass and/or stainless steel probes
Whatman thimble, single thickness, 43 mm x 123 mm, and holder
Connecting tubing
Alundum thimble, porosity RA 98 coarse, 45 mm x 127 mm, and holder
Vacuum pump, or air aspirator, with flow control valve
Seven 500-ml Greenburg-Smith impingers and ice bath containers
Two integrating-type dry gas meters fitted with mercury manometers and thermometers
Twelve evacuated 2-liter round-bottom flasks
Pitot tube and inclined manometer
Thermocouple pyrometer
Gas sample collecting bottle, 5-liter, (for Orsat analysis)

Outline of Sampling Method

Sampling for particulate matter, ammonia, oxides of sulfur, and organic acids was carried on simultaneously and continuously for a period of 1 hour or more with two sampling trains. A gas sample for Orsat analysis was

Figure 3. Source testing team with truck and equipment necessary for two stack tests.

collected by a liquid displacement method. During the sampling period, grab samples for aldehydes, oxides of nitrogen, and hydrocarbons were taken.

The sampling trains were assembled as shown in Figure 4.

The probes were placed within the stack with the thimble holders outside the stack. The thimble holders were insulated with asbestos cloth, to keep the temperature within the holder above the dew point* of the stack gases. The temperatures of the thimbles were sufficiently low (about 200°F.) to permit collection of sulfuric acid aerosol.

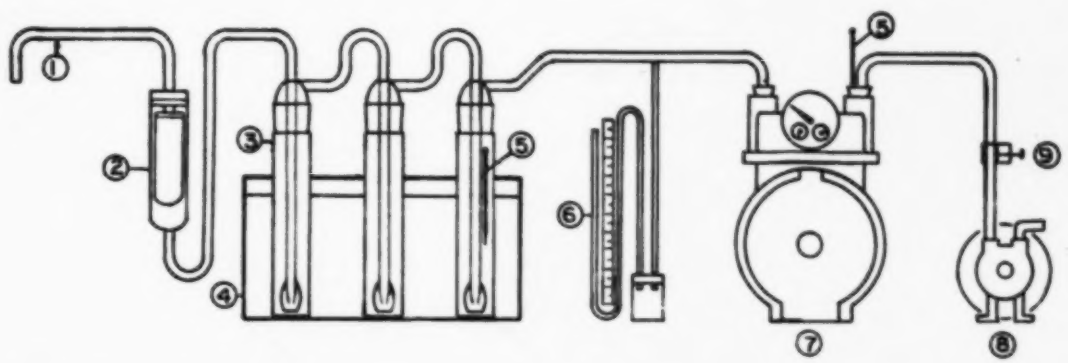

Figure 4. Schematic drawing of train for sampling combustion gases.

The two trains following the sampling probes were (see Figure 4):

A. An Alundum thimble 2 with a pyrex glass wool lining followed by four 500-ml. impingers 3 immersed in an ice bath 4. The first two impingers each contained 100 ml. of distilled water. The third impinger contained 100 ml. of a 5 per cent HCl solution. The last impinger was dry and fitted with a thermometer 5. The impinger section was followed by a manometer 6, meter 7, and vacuum pump 8. A hose clamp 9 was used to control the gas flow rate. Figure 6 shows an assembled Alundum thimble train. Either Vycor or Pyrex glass, or stainless steel sample probes may be used.

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*In this discussion the term dew point refers to the temperature of condensation of water vapor only.

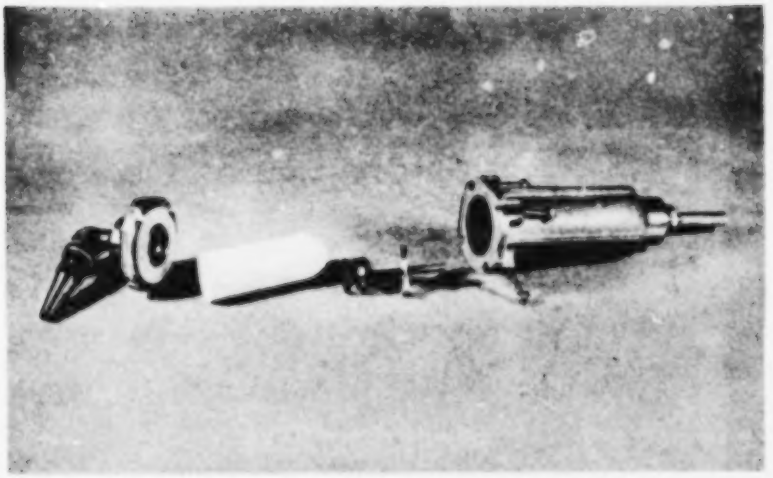

Figure 5. Alundum thimble and disassembled holder. Sampling nozzle is shown inserted in holder cap. During the test the nozzle was placed at the end of the sampling probe.

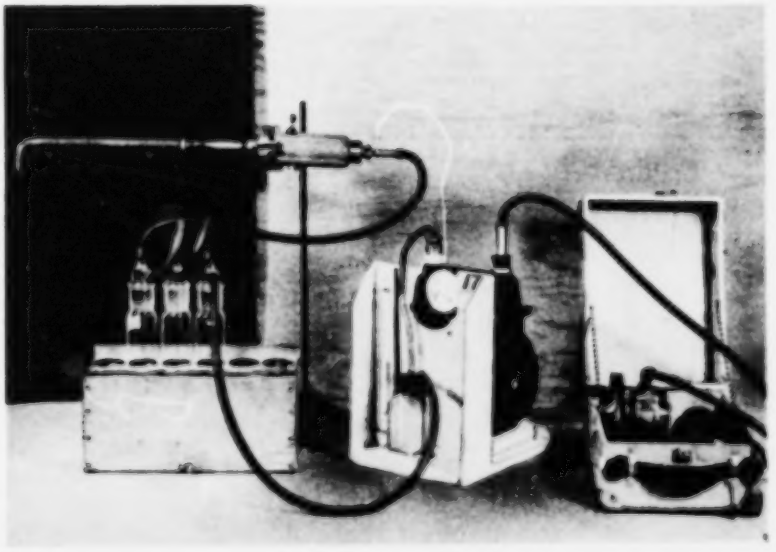

Figure 6. Alundum thimble sampling train provided with Vycor glass sampling probe.

B. A single thickness Whatman paper thimble 2 followed by three 500-ml. impingers 3 immersed in an ice bath 4. The first two impingers each contained 100 ml. of a 5 per cent NaOH solution. The third impinger was dry and was provided with a thermometer 5. Following the impinger section was a manometer 6, a meter 7, and a vacuum pump 8.

Two sampling trains were used for the determination of the following:

Particulate matter - Alundum thimble catch and material filtered from H_2O and HCl impinger solutions.

NH_3 - H_2O and HCl impinger solutions.

SO_3 - Whatman thimble catch

SO_2 - NaOH impinger solutions

Organic acids - NaOH impinger solutions

An integrated gas sample for Orsat analysis (carbon monoxide, carbon dioxide, and oxygen) was collected by withdrawing gases continuously from the stack at a constant rate by liquid displacement. A 5-liter bottle filled with a saturated sodium sulfate solution, slightly acidified with sulfuric acid, was used as the gas holder (see Figure 7).

As the solution siphoned out, the gas sample was drawn into the bottle. The rate of siphoning was adjusted so that a gas sample of about 4 liters was obtained during the course of the test. The sample was drawn from the same stack or breeching cross section used for collecting the other constituents.

During the sampling period, four grab samples (see Figure 8) of each of the following were taken at equal intervals:

Aldehydes: A gas sample was drawn into a 2-liter evacuated flask containing 10 ml. of a 1 per cent solution of sodium bisulfite.

Oxides of Nitrogen: A gas sample was drawn into a 2-liter evacuated flask containing 25 ml. of a solution of hydrogen peroxide and sulfuric acid. The absorbing solution was prepared by adding 1 to 2 ml. of 3 per cent H_2O_2 to 100 ml. of 0.1N H_2SO_4.

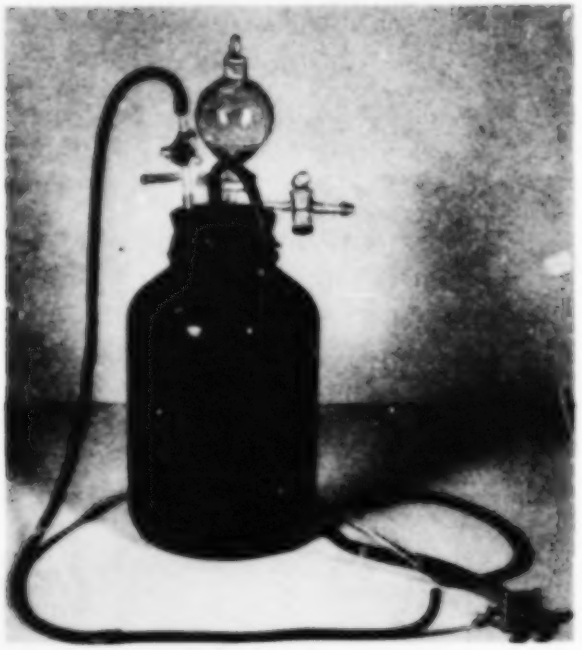

Figure 7. Bottle used to collect stack gases for Orsat analyses.

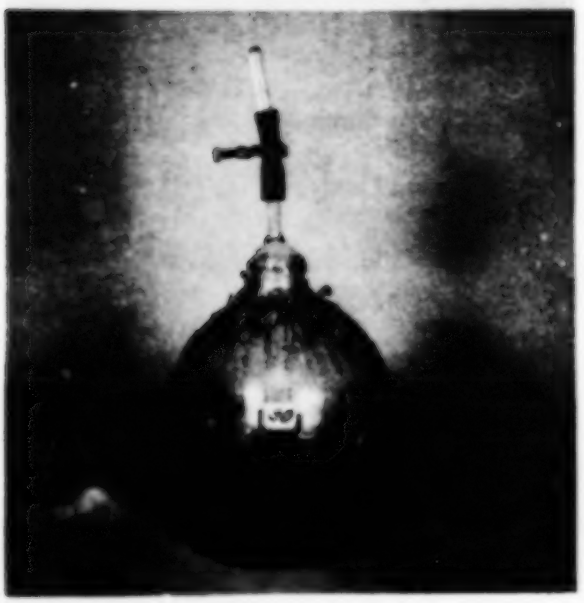

Figure 8. Two-liter grab sample bulb.

Hydrocarbons: A gas sample was collected in a dry evacuated 2-liter flask. This sample was analyzed by infrared spectrophotometry.

OUTLINE OF ANALYTICAL METHODS

Many of the analytical methods used are standard and commonly employed in routine laboratory analysis. The following is an outline of the analytical methods used during this testing program.

Alundum Thimble

The nozzle was brushed out and the contents added to the thimble. The thimble and contents were heated for one-half hour at 105° C., cooled in a desiccator for one-half hour and weighed. The difference from the tare weight represented the weight of particulate matter collected by the thimble.

Impinger Train (Water-HCl)

The increase in volume of the impinger solutions was measured and, with the temperature and pressure of the saturated gas leaving the last impinger, was used to determine the per cent moisture in the stack gas. The data were also used for calculations of total sample volume. The impinger solutions were filtered and the residues weighed. The weight of insolubles in the impinger solutions were added to the thimble catch to give the total weight of particulate matter collected. An aliquot of each of the water and HCl portions was analyzed for ammonia by the Nessler method (5).

Whatman Paper Thimble

The sulfuric acid aerosol collected was extracted with distilled water and titrated to the methyl orange end point. The results were reported as SO_3. As a check, sulfate was determined gravimetrically on the same solution (Appendix). Results were in good agreement.

Impinger Train (5 Per Cent NaOH)

The impinger solution was used for two determinations:

Sulfur Dioxide. An aliquot was oxidized and the sulfur determined gravimetrically. Results were reported as SO_2 (Appendix).

Organic Acids. An aliquot was acidified and ether extracted. The organic acids in the ether layer were titrated with standard sodium hydroxide solution. Results were reported as acetic acid (Appendix).

Integrated Gas Sample for Orsat Analysis

The 3 to 4-liter sample was analyzed on a standard Orsat type apparatus for CO_2, O_2, CO, and N_2 by difference. Carbon monoxide was found to be too low to be measurable by Orsat analysis, and was measured with a Mine Safety Appliances Co. carbon monoxide analyzer sensitive to concentrations as low as 0.001 per cent.

Grab Samples

Aldehydes. The sodium bisulfite-aldehyde complex was determined by an iodine titration (6). Results were reported as formaldehyde.

Oxides of Nitrogen. The absorbing solution was made alkaline and evaporated to dryness. Phenoldisulfonic acid solution was added to the residue and the determination of the total oxides of nitrogen was made by measuring the light absorption of the resulting yellow solution in a photoelectric colorimeter. Results were reported as NO_2 (7).

Hydrocarbons. The gas sample collected in the 2-liter dry evacuated flask was purged into an infrared spectrophotometer and analyzed for total hydrocarbons by scanning between 3 and 4 microns. The instrument is calibrated for normal hexane at 3.45 microns (8).

Fuel Analysis

Fuel Gas. Fuel gas samples were analyzed at the refineries by mass spectrometer to give the percentage composition. The information was used for calculations of stack gas volumes when direct measurements were lacking.

Fuel Oil. Fuel oil samples were analyzed for total carbon, hydrogen, and sulfur by combustion methods. The data were used for calculation of stack gas volumes when needed, in conjunction with corresponding fuel gas analyses.

DATA EVALUATION

Total Emissions from Boilers and Process Heaters

The emissions of air contaminants from combustion of fuel in boilers and process heaters are dependent on several factors. Emissions of sulfur oxides are a direct function of the composition of the fuel, while the emissions of the other contaminants are primarily influenced by combustion temperature, heater design, or air-fuel ratio, rather than fuel composition.

The selection of the units tested had to be based mostly on their accessibility and adequacy of sampling facilities. In general, they reflected an average of the various design configurations and operating conditions in local refineries. The composition of the fuel burned in these heaters, however, was not representative of the average of all the fuel burned throughout the refineries.

Emissions of oxides of sulfur were measured from these units to establish the average ratio of SO_3 to SO_2 in the stack gases, which is essentially independent of the sulfur content of the fuel. While the measured values of SO_2 agreed with values calculated from the fuel analyses supplied by the refineries, they could not be expanded to yield total emissions of sulfur oxides because the fuel did not have the same sulfur content as the average of all fuels burned. Instead, data on average fuel composition and consumption for all refineries had to be used. These data were made available to the Joint Project from a special semi-annual survey of sulfur dioxide emissions conducted by the Los Angeles County Air Pollution Control District and were used to calculate total sulfur oxide emissions as SO_2.

Analyses of stack gases for SO_3 were made in tests on ten gas burning units and on six furnaces fired with both gas and oil. Comparison with the measured SO_2 emissions from these units gave an average ratio of SO_3 to total sulfur as SO_2 of 0.03 for both gas and mixed fuel combustion. Using this ratio, the total emissions of SO_3 and SO_2 were determined from the calculated total sulfur oxides emissions.

Average emissions for each of the other contaminants per unit of fuel burned were calculated from the test data for both oil and gas, and applied to the total fuel usage to arrive at the total emission rates. Tables IV and V show the average emissions per unit of fuel burned. The total emission rates are presented in Table VI.

Of the 20 tests made for carbon monoxide, 14 were negative, five showed a trace less than 0.001 per cent, and one showed a concentration of 0.003 per cent. These results indicate that the emission of carbon monoxide from boilers and process heaters was negligible.

Analytical Methods

The concentrations of the various contaminants found in combustion gases with the exception of oxides of nitrogen and SO_2 were very low and approached the limit of sensitivity of the available analytical techniques. The data for hydrocarbons and aldehydes include a number of tests which showed the presence of the contaminant, but in concentrations below the quantitative range of the analytical technique. In these cases a concentration was assigned equal to the lower limit of the analytical method. The values are noted as maximums in the tables.

The infrared spectrophotometer used to analyze for hydrocarbons is calibrated for hexane and gives low results for the lower molecular weight hydrocarbons (9). During two tests on heaters samples of stack gases were analyzed for hydrocarbons using both infrared and gas chromatographic techniques. In both cases the infrared technique reported less than 5 ppm. of hydrocarbons as hexane. The gas chromatograph showed 5 ppm. of C_3 and 20 ppm. of C_2. The concentration of methane was below the limit of sensitivity of the method (100 ppm.).

Average Emission Factors

The average emission factors for gaseous fuels are shown in Table IV. These are calculated by dividing the total emissions of each contaminant in pounds per hour for all tests by the amount of gas burned in all tests in MCFH. Since no tests were made on units burning only oil, emission factors for oil combustion could not be determined directly. The emissions resulting from the gas being burned along with the oil were subtracted from the total emissions before calculation of the factors for oil. Average emissions from the combustion of fuel oil are shown in Table V and were

Table IV

AVERAGE EMISSIONS PER UNIT OF GASEOUS FUEL BURNED IN BOILERS AND PROCESS HEATERS

Contaminant	No. of tests	Fuel, MCFH	Emissions, lb./hr.	Emission Factor lb./MCF
Hydrocarbons, as hexane by I.R.	14	1240.8	32.7*	0.026
Oxides of nitrogen, as NO_2	14	1240.8	287.5	0.23
Particulate matter	3	218.5	4.6	0.021
Ammonia	7	600.8	0.22	0.00036
Aldehydes, as HCHO	14	1240.8	3.8*	0.0031
Organic acids, as acetic acid	14	1240.8	17.4	0.014

* These are maximum values. The concentrations encountered in some of the tests contributing to this total were below the sensitivity of the analytical technique.

calculated using the following formula:

$$e_o = \frac{E - (e_g F_g)}{F_o}$$

e_o = emission factor for oil, pounds per gallon.

E = total emissions, all units tested, pounds per hour.

e_g = emission factor for gas, pounds per MCF.

F_g = total gas burned in all tests, MCFH.

F_o = total oil burned in all tests, gallons per hour.

The factors for both oil and gas are gross averages weighted for the amount of fuel used.

Table V

AVERAGE EMISSIONS PER UNIT OF FUEL OIL BURNED IN BOILERS AND PROCESS HEATERS

	No. of Tests	Fuel used		Emissions, Pounds/hour			
		Gas MCFH	Oil gal./hr.	Total	From gas burned**	From oil burned	Factor, pounds/gal.
Hydrocarbons, as hexane by I.R.	6	275	2724	16.4*	7.2	9.2*	0.0034
Oxides of nitrogen, as NO_2	6	275	2724	250.5	63.6	186.9	0.068
Particulate matter	3	166	1548	32.3	3.5	28.8	0.019
Ammonia	5	246	2598	0.36	0.09	0.27	0.0001
Aldehydes, as HCHO	6	275	2724	2.4*	0.8	1.6*	0.0006
Organic acids, as acetic acid	6	275	2724	34.8	3.8	31.0	0.011

* These are maximum values. The concentrations encountered in some of the tests contributing to the total were below the sensitivity of the analytical technique.

** These values were calculated by multiplying the amount of gas burned by the emission factors for gaseous fuel shown in Table IV.

Table VI

TOTAL EMISSIONS FROM BOILERS AND PROCESS HEATERS IN REFINERIES IN LOS ANGELES COUNTY

Contaminant	Emissions, tons per day		
	Fuel gas*	Fuel oil*	Total
Hydrocarbons, as hexane by I.R. (max.)	4.5	0.3	5
Sulfur dioxide	48	24	72
Oxides of nitrogen, as NO_2	40	6	46
Particulate matter	3.4	1.7	5
Sulfur trioxide	1.4	0.7	2
Ammonia	0.06	0.01	<0.1
Aldehydes, as HCHO (max.)	0.5	0.05	0.5
Organic acids, as acetic acid	2.5	1	3.5

* Daily average gas and fuel oil usage for two months, July 1957 and January 1958 was 340 million cubic feet of gas and 4300 barrels of fuel oil.

Relative Losses from the Combustion of Oil and Gas

A comparison was made of the emissions from the combustion of an equivalent amount of gas and fuel oil. The conversion to a common Btu. output was made using 1100 Btu. per cubic foot as the heating value for gas, and 150,000 Btu. per gallon for oil. This comparison for the various contaminants is shown in Table VII. The results indicate that emissions are greater from the combustion of oil, especially for organic acids and particulate matter.

Comparison of Emissions from a Fume Burner and Boilers and Heaters

Tests were made on a fume burner used to incinerate the odorous effluent gases from an asphalt air blowing unit. The furnace burned 7600 CFH of natural gas and incinerated the combustibles in 48,000 CFH of effluent air from the blowing operation. This effluent air, analyzed on a mass spectrometer, contained less than 1 per cent of organic compounds. As

Table VII

RELATIVE EMISSIONS FROM BURNING OF OIL AND GAS

Contaminant	Emission Factor, Pounds per 10^6 Btu.*		Ratio, Oil to Gas
	Gas	Oil	
Hydrocarbons, as hexane by I.R.	0.024	0.022	0.9
Oxides of nitrogen, as NO_2	0.21	0.44	2.1
Particulate matter	0.019	0.12	6.3
Ammonia	0.00033	0.00065	2.0
Aldehydes, as HCHO	0.0028	0.0039	1.4
Organic acids, as acetic acid	0.013	0.072	5.5

* Conversion from volumes of gas and oil was made using values of 1100 Btu. per cubic foot of gas and 150,000 Btu. per gallon of oil.

shown in Table VIII the fume burner emitted less than the average amount of oxides of nitrogen, but from 20 to 100 times as much hydrocarbons, organic acids and aldehydes as an equivalent amount of fuel burned in a boiler or process heater.

Table VIII

COMPARISON OF EMISSIONS FROM BOILERS AND HEATERS AND A FUME BURNER

Contaminant	Fume Burner, Pounds per MCF of Fuel	Boilers and Heaters Pounds per MCF of Fuel
Hydrocarbons, as hexane by I.R.	0.52	0.026
Oxides of nitrogen, as NO_2	0.08	0.23
Ammonia	0.0005	0.00036
Aldehydes, as HCHO	0.31	0.0031
Organic acids, as acetic acid	0.39	0.014

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ANALYTICAL METHOD FOR OXIDES OF SULFUR

Scope

This method is used for the determination of oxides of sulfur in the Whatman paper thimble and the 5 per cent NaOH impinger solutions.

Outline of Method

Sulfur trioxide is extracted from the paper thimble with hot water and determined by titration. As a check, sulfate is determined gravimetrically on the same solution. Sulfur dioxide collected in the impingers is oxidized with bromine and determined gravimetrically as barium sulfate.

Reagents

Bromine water

Hydrochloric acid, concentrated

Barium chloride solution, 10 per cent

Silver nitrate solution

Procedure

Dilute a 100-ml. aliquot of the combined impinger solutions from the 5 per cent sodium hydroxide sampling train to 200 ml. Add bromine water in slight excess (until color remains) to oxidize the SO_2. Boil for

a few minutes. Neutralize with concentrated hydrochloric acid and add 2 ml. excess. Boil to remove excess bromine. Filter to remove any silica or other solid material. Heat to boiling and add 10 per cent barium chloride solution with constant stirring until an excess is present. Digest the solution for 1 hour over a steam bath. Filter through a prepared Gooch crucible, checking the filtrate for complete precipitation. Wash with hot water until the filtrate is free of chloride as determined by adding silver nitrate solution to the washings. Transfer the crucible to a muffle furnace and ignite to constant weight at 750°C.

The water extract of sulfur trioxide from the Whatman thimbles is determined as above with the exception that bromine oxidation is omitted.

Calculations

The weight of SO_2 is determined as:

$$\text{grams } SO_2 = 0.2744 \text{ grams Ba } SO_4$$

The weight of SO_3 is determined as:

$$\text{grams } SO_3 = 0.3430 \text{ grams Ba } SO_4$$

ANALYTICAL METHOD
FOR
ORGANIC ACIDS

Scope

This method is used for the determination of organic acids collected in the 5 per cent NaOH impinger solutions.

Outline of Method

The alkaline absorbing solution is acidified and the liberated organic acids extracted with ether and determined by titration with standard alkali.

Apparatus and Materials

Liquid-liquid extraction apparatus, medium size,
as Corning No. 92232 or equivalent
Glas-col 500-ml. mantle and rheostat
pH meter

Reagents

Phenolphthalein indicator

Sulfuric acid, reagent grade

Sodium hydroxide solution, 0.1N

Ethyl ether, peroxide-free and acid-free

Procedure

An aliquot of the sodium hydroxide absorbing solution is transferred to a beaker. The beaker is placed in an ice bath and allowed to come to equilibrium temperature after which it is covered with peroxide-free, acid-free ethyl ether.

Concentrated sulfuric acid is added dropwise to the beaker with constant stirring until a pH of 2.0 is attained as determined with an external indicator, preferably a pH meter.

The acidulated absorbing solution is then transferred to a liquid-liquid extractor. The transfer is facilitated with the aid of a long stemmed funnel which serves to introduce the sample into the extractor without splashing droplets in the side arm. The final level of the aqueous layer should be approximately 2 inches below the level of the side arm. The inner tube of the extractor is lowered into position and a 500-ml. short-neck round-bottom flask, containing 250 ml. of ether, and an ebulator is attached to the side arm.

The apparatus is then placed in the hood, fastened in place with a heating mantle under the flask, and the reflux condenser connected. The ether flask is heated in the mantle so that vigorous boiling is attained and ether is being condensed rapidly, dropwise, from the reflux condenser into the inner extractor tube.

The extraction is continued for a total of 8 hours (about 85 liters of ether will pass through the apparatus during this time).

After the elapsed extraction time, the apparatus is allowed to cool and the condenser removed. The entire apparatus is carefully tilted to permit most of the ether layer in the extractor to flow into the flask without permitting any of the aqueous layer to also flow into the flask. The flask is disconnected, the ebulator removed, and the contents transferred to a separatory funnel. It will be noted that a small aqueous portion is present in the ether. This portion is carefully drained off and discarded. Approximately 40 ml. of distilled water plus three drops of phenolphthalein are added to the separatory funnel. The solution is titrated in the funnel with 0.1N NaOH until, after vigorous shaking, a pink color persists.

A blank determination is performed in exactly the same manner, a

portion of the prepared impinger solution being retained, acidulated, extracted, etc., for this purpose. The reagent blank determination must be performed.

Calculations

The blank titration (ml.) is subtracted from the sample titration. Calculations are normally based upon acetic acid values, hence:

$$\text{grams acetic acid} = (\text{ml. NaOH})\,(N)\,(0.06)$$